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THE AGE AND ORIGIN OF THE GYPSUM DEPOSITS OF CENTRAL IOWA

A DISSERTATION

SUBMITTED TO THE FACULTY OF THE OGDEN GRADUATE SCHOOL
OF SCIENCE, IN CANDIDACY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

(DEPARTMENT OF GEOLOGY)

BY
FRANK ALONZO WILDER

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THE AGE AND ORIGIN OF THE GYPSUM DEPOSITS OF CENTRAL IOWA.

THE known gypsum of Iowa is confined to Webster county, which lies somewhat north and west of the center of the state. Here it occupies a tract about six miles wide and fifteen miles long, on the edge of which the city of Fort Dodge is located. The original gypsum area has been greatly reduced by the erosive and solvent action of the Des Moines River, which crosses it nearly at right angles, cutting completely through it and deep into the Coal Measures beneath. Some of the earliest geological work undertaken in the state was carried on in this region. The Des Moines River exposes along its banks the indurated rock and gives at times sections of rock and drift 200 feet in thickness, which greatly facilitate geological study. The unique deposit of gypsum has been attractive to the student on account of the theoretical problems that it presents, and to others it is interesting on account of its practical value.

In the year 1849 Owen[1] made a hurried trip up to the Des Moines River, noticed the gypsum, and made certain deductions in regard to its origin. After describing its remarkable thickness and purity, he adds:

> This plaster stone of the Des Moines does not appear to have been deposited in nests or conical heaps, as in the shales of the Onondago Salt Group of New York, but rather in continual horizontal beds, conformable to the underlying shale. The immense quantity of gypsum of this part of the

[1] *Geology of Wisconsin, Iowa, and Minnesota*, p. 126 (Philadelphia, 1852).

upper Des Moines can hardly be accounted for on the principle of double chemical decomposition between sulphate of iron and carbonate of lime, formerly existing where the plaster now is, since there does not appear to be an equivalent bed of iron in the vicinity, nor yet beds of limestone, except thin bands of black bituminous, calcareous rocks, by no means extensive, that are in immediate connection with the plaster-beds. It seems rather to have been an original deposit at the bottom of the ocean; the sulphate of lime having probably been derived, during the formation of the rocks, from submarine sources.

In 1856 Worthen[1] visited the region and came to the conclusion that the gypsum does not lie conformably on the Coal Measures. Hall[2] in 1858 and McGee[3] in 1884 considered the stratigraphic relationship and age of the gypsum. Webster county was included in the geological studies of C. A. White and references to coal and gypsum are made in his annual reports of 1868 and 1870.[4] In these reports White pointed out the great value of the Webster county gypsum, and urged that it be developed so that the state might furnish the stucco and land plaster used within its borders.

Keyes[5] reported quite fully on the gypsum area in 1893, describing the position and the extent of the deposit and its stratigraphic relationships, and with reference to its age concluding that it should be referred to the Cretaceous.

GENERAL RELATIONS OF STRATA.

Excepting limited Carboniferous outliers, Webster county contains the most northern of the Iowa Coal Measures. These lie just beneath the drift throughout the southern part of the county, and extend north to a point three miles above Fort Dodge. The Saint Louis limestone underlies the drift in the northern part of the county, and appears along the Des Moines well to the south, where the stream has cut through the Coal Measures. Upon the Coal Measures in the central part of the county lie the gypsum beds unconformably. The term "gypsum

[1] *Geology of Iowa*, Vol. I (1858), p. 177. [2] *Ibid.*, p. 142.

[3] *Tenth U. S. Census*, Vol. X, "Building Stones," p. 258 (Washington, 1884).

[4] *First Annual Report State Geologist* (1868), pp. 25–27; *Second Annual Report* (1868), pp. 135–40. *Geology of Iowa*, Vol. II, pp. 293, 254–56.

[5] *Iowa Geological Survey, Annual Report*, Vol. III (1893), pp. 259–304.

beds" includes the gypsum, red shales, and sandstone which often overlie it, and three or four feet of fine clay which commonly occur at its base. Two sections may be given to illustrate their stratigraphic relationships.

The exposure at what was formerly known as Kohle's Brewery near the mouth of Soldier Creek and within the Fort Dodge city limits has long been regarded as typical for the gypsum and associated red shales and sandstone.

		Feet
9.	Gravel, fresh, clean, well water-worn, containing much limestone	5
8.	Drift, slightly oxidized, unleached	28
7.	Gravel, rusted, many decayed fragments, showing only at certain points along bluff	2
6.	Sandstone, soft, friable, buff-colored, though at points not far away it is white and heavily bedded	5
5.	Shales, argillaceous, sandy layers alternating	5
4.	Sandstone, buff, friable	2
3.	Shale, gray	2
2.	Thin bands of gypsum and shale	7
1.	Gypsum, massive, exposed	11

SECTION IN THE PIT OF THE FORT DODGE CLAY WORKS.

3.	Drift, yellow, unleached, lower part a little darker than the upper	35
2.	Red sandy shale, with occasional thin bands of sandstone	0–10
1.	Gray Coal-Measure shales, often containing fossils of ferns, lepidodendrons. A few iron nodules present and crystals of selenite. Separated from red shales above by sharp line of unconformity. Along the line of separation there is a layer of gumbo, one foot thick	30

No. 2 includes the red shales found in so many places above the gypsum. These red sandy shales are so characteristic, and associated so conformably with the gypsum, that in this section, as elsewhere, they may safely be regarded as of the same age as the gypsum.

NATURE OF THE GYPSUM BEDS.

All of the gypsum in Webster county, except the scattered crystals of selenite in the Coal-Measure shales, is stratified in heavy layers which are rarely less than six inches thick, commonly twelve inches or more, attaining a maximum thickness of two feet. The layers are separated by traces of clay. In thick-

ness the deposit varies from ten to thirty feet. Instead of thinning out gradually through a considerable area, it seems to diminish but slightly before it abruptly gives place to shale. At Kohle's Brewery, for instance, ten feet of gypsum appear, while half a mile further north, in the clay pit of the Fort Dodge Brick & Tile Co., only drift and Coal Measure shales are found. Everywhere in the Webster county gypsum the laminæ alternate regularly in color from green to white. The gypsum is remarkably pure calcium sulphate ($CaSO_4 2H_2O$). The lower layers, generally the lower three feet, are not as pure as the upper and are not used in the manufacture of plaster. Even in these lower layers, however, the amount of the impurities is so small that they would hardly injure the plaster. An analysis of the upper layers shows:[1]

Calcium sulphate ($CaSO_4$,	78.44
Water crystallization (calculated)	20.76
Insoluble matter (impurities)	0.65

An analysis made by Professor J. B. Weems of gypsum taken from the lower, middle, and upper part of those layers that are rejected in making plaster shows:

Silicia, SiO	1.92
Alumina, $A_{12}O_3$	1.00
Calcium sulphate, $CaSO_4$	76.28
Water	20.72
Total	99.92

With traces of magnesia and carbon dioxide.

When made into plaster this lower layer, while soft, will not adhere to the laths satisfactorily. After hardening it is as firm and durable as the plaster made from the upper layers. The gypsum is crystalline throughout, the slender needlelike crystals being arranged at right angles to the plane of sedimentation. Though the gypsum is now well preserved by the thick mantle of drift that overlies it, at one time it formed the surface rock, and in consequence suffered considerably from erosion and solution. When the overlying drift is removed, the surface of the gypsum everywhere seems deeply trenched, some of the trenches

[1]Analysis by G. E. PATRICK, *Iowa Geological Survey*, Vol. III, p. 291.

cutting half-way through the entire deposit. At times the gypsum is wholly cut out, and records of drillings at points wholly surrounded by gypsum show only gravel. Trenches are frequently encountered in mining the gypsum when they cause considerable trouble. Where exposed along ravines, the gypsum is decayed on the surface to a depth of three or four inches, and picturesquely grooved and fluted.

AGE OF THE GYPSUM AND ASSOCIATED DEPOSITS.

In considering the age of the gypsum, the red shales which accompany it must be kept in mind, for they are very closely associated, as shown by exposures along Soldier Creek, where thin layers of gypsum are found in the shales. Wherever they were not removed by preglacial erosion, these shales overlie the gypsum conformably. Their extent is greater than that of the gypsum, and in the pit of the Fort Dodge clay works, as already described, they may be seen resting unconformably on the Coal Measures. In Douglas township, sec. 8, there is a good exposure of these red shales which is six miles northwest of any known gypsum. Their color is striking, often brilliant, and for this reason they have been used to some extent as a natural pigment.

The fact that the gypsum and the red shales lie unconformably on the Coal Measures is good ground for believing that, if they belong to the Paleozoic era, they were formed near its close, during the Permian. The Permian beds of Kansas, Indian Territory and Texas, which contain quantities of gypsum, are so highly and so characteristically colored that they are known as the "red beds." These red beds, like the red shales and gypsum of Iowa, are nearly destitute of fossils, due probably to the fact that the climatic conditions favoring deposition of gypsum were hostile to organic life. Aridity is the climatic characteristic most essential for great deposits of gypsum, and the redness of the sandstones and shales usually accompanying gypsum deposits of all ages and localities may fairly be assumed to be an effect of climate, direct or indirect, on the iron content of the soil. All of these considerations—namely, the arid climate that prevailed during the Permian, shown by great gypsum deposits associated

with red shales occurring in both Europe and America, and the striking resemblance which the series bears to the Permian only 300 miles to the west—carry great weight. The Iowa series might reasonably be interpreted as an outlier of the Permian of Kansas and Indian Territory. During the long interval between its deposition and that of the drift which now protects it erosion had an abundant opportunity to remove the Permian from the intervening territory. The gypsum was doubtless protected by heavy beds of the red shales, for, had it been exposed long, it must have yielded to the solvent and erosive action of water.

The gypsum has been referred to the Cretaceous and to the Eocene for stratigraphic reasons. In the region of the Mississippi valley and great plains there are two well-marked unconformities to be considered. One occurs at the base of the Cretaceous, and the other at the base of the Eocene. By an unconformity also, the gypsum beds of Iowa are separated from the Coal Measures. The Missourian, which farther west attains a considerable thickness, is here wholly absent, and instead of deposition, erosion was probably taking place in the Fort Dodge region during this stage. No unconformity has been recognized between the Permian and the Coal Measures in Texas and Kansas. The absence of an unconformity in these regions does not preclude the possibility of a local unconformity in Iowa. More striking unconformities, local in nature, between certain of the older formations in the state, can be positively demonstrated. The surface beneath the gypsum was plainly not brought down to a base level before the deposition of the gypsum, for the gypsum lies in an erosion trough which has rather steep slopes.

In view of the important climatic conditions which will be presently considered, which seem to have been particularly favorable during the Permian all over the world, a local unconformity may be admitted if it obviates the necessity of referring the gypsum to the Cretaceous, where these conditions were notably absent.

To regard the gypsum as belonging to the Eocene seems impossible, when the conditions under which it was formed, considered in a later paragraph, are taken into account. The evi-

dence seems sufficient to show that a deposit so extensive and so pure could not have been formed in a basin without oceanic connection, and an oceanic connection during the Eocene for a basin in central Iowa seems impossible.

Attention has lately been called to a well boring at Cherokee which reached a depth of 800 feet. At the bottom, beneath a sandstone that was certainly Dakota, and at a depth below any possible Cretaceous beds in this state, sixteen feet of gypsum are said to have been found. The persons making the report are regarded as reliable. Gypsum is readily identified and the report has significance. An effort is being made to determine positively the nature of the material regarded as gypsum. If the report is correct it has a direct bearing on the question in hand, for the position of this gypsum would indicate that it belonged to the close of the Carboniferous.

The claims of the Cretaceous have been pressed also, on other than stratigraphic grounds.[1] Reference to the geological map of Iowa shows that Cretaceous deposits are present throughout the greater part of northwestern Iowa, and that they approach within thirty miles of Webster county, at Auburn in Sac county, where they appear as chalk. The Cretaceous in Iowa consists of sandstone of the Dakota stage, and shales, limestone and chalk of the Colorado stage. Sandstone, shales, and limestone have yielded abundant fossils which definitely fix their age. Other things being equal, it would be somewhat more natural to regard the Webster county gypsum series as an outlier of the Cretaceous than of the Permian which is farther away, yet the distance is not so great as to render a correlation with the Permian in any degree improbable, if the preponderance of other evidence favors such a view. A review of Cretaceous climatic conditions is first of all necessary, for if aridity is a more striking characteristic of the Permian than of the Cretaceous, the Cretaceous age of the gypsum can hardly be established. The Dakota sandstone is at times red, but this color does not everywhere prevail, and it does not characterize the Cretaceous shales and limestones in any degee. The Dakota sandstone abounds in fossils, as does the

[1] *Iowa Geological Survey*, Vol. III, p. 290.

limestone of the Colorado stage, in which *Inoceramus labiatus* is found in great numbers. The Benton shales, while not so rich in fossils as the limestones, contain *Ostrea congesta*, *Prionocyclus wyomingensis*, and other species, none of which are brackish water forms. They contain also some selenite, but, in view of the fossil content of the shales, it is probable that the selenite was not formed by precipitation from concentrated brine at the time that the shales were laid down, but is due to subsequent chemical reaction in which sulphuric acid, generated perhaps from iron pyrites, converted part of the lime carbonate of the shales into the sulphate. In barrenness of fossils, in color, and in association with gypsum the red shales which accompany the Iowa gypsum resemble the Permian of Kansas much more than they do the Cretaceous shales of Iowa. The presence of chalk in Sac county, close to what must have been the Cretaceous shore indicates that for a time sediments from land were at a minimum, and organic sediments unmixed with land waste were able to accumulate near the shore. This would indicate an absence of the barren surface usually attending aridity, or the absence of elevation, or both, so that climatic conditions favoring deposits of gypsum are not implied by the chalk of the Cretaceous. Regions devoid of rainfall are characterized by wind storms of great violence capable of transporting much earthy material as dust and carrying it out to sea, where it would ultimately be deposited. The arid regions of America are subject to brief but violent rain storms, during which erosion is vigorous on the surface barren of vegetation. Low land surfaces covered with an abundant vegetation are most favorable for pure chemical and organic accumulations in the neighboring seas. The great purity of many gypsum deposits presents a difficulty for this very reason, for land vegetation must have been limited during the concentration of the sea water and conditions favorable for dust storms seem likely to have prevailed. Microscopic examination of the Iowa gypsum reveals particles of sand scattered through the gypsum, probably by wind, but the total amount is small, amounting to about 1 per cent. of the whole.

The age of the great gypsum and salt deposits of the world is shown below:

FOREIGN.	AMERICAN.
PLEISTOCENE AND RECENT.	
Caspian Sea and Asiatic lakes.[1]	Great Salt Lake.
PLIOCENE.	
Transylvania, near Prague (salt).[2]	
Caspian Sea in Karabhogas Bay (salt and gypsum).[3]	
Austria at Wieliczka, Siebenbürgen (salt and gypsum).[4]	
MIOCENE.	
None.	
OLIGOCENE.	
Transylvania and Carpathian Mountains (gypsum and salt).[5]	
Germany, Sperenberg (gypsum).[6]	
France, Montmartre (gypsum).[7]	
EOCENE.	
None.	
CRETACEOUS.	
None.	
JURASSIC.	
None.	
TRIASSIC.	
Germany:[8]	Black Hills (gypsum).[10]
Hanover, Arnstadt.	
Erfurt, Thuringia.	
Lothringen (gypsum and salt).	
England:[9]	
From Scotland to Devonshire (gypsum and salt).	

[1] GEIKIE, *Text-Book of Geology*, 3d ed., pp. 737–39.

[2] *Ibid.*, p. 1018.

[3] *Ibid.*, p. 1004.

[4] CREDNER, *Geologie*, pp. 699, 700.

[5] GEIKIE, *op. cit.*, p. 993.

[6] CREDNER, *op. cit.*, p. 679.

[7] *Ibid.*, p. 675.

[8] *Ibid.*, p. 520.

[9] GEIKIE, *op. cit.*, p. 866.

[10] U. S. Geological Survey, DARTON's report on Black Hills, *Twenty-first Annual Report*, Part IV.

PERMIAN.

Germany:[11]
The Hartz (gypsum).
Stassfurt, Sperenberg (gypsum and salt).
South Tyrol (gypsum).
Russia (gypsum, salt).[12]

Iowa (gypsum).
Texas (gypsum).[13]
Kansas (salt and gypsum).[14]
Oklahoma and Indian Territory.[14]
Black Hills (gypsum)[15]

CARBONIFEROUS.

Lower Carboniferous.
Mississippian.
Lower Michigan (gypsum).[16]
Nova Scotia (gypsum and salt).[17]
Virginia (gypsum and salt).[18]
Montana (gypsum).[19]

DEVONIAN.

None.

SILURIAN.

Russia, Baltic provinces (gypsum).[20]

New York (gypsum and salt).[21]
Ohio (gypsum and salt).[22]
Pennsylvania (gypsum).[23]
Upper Michigan (gypsum).[24]

ORDOVICIAN.

None.

CAMBRIAN.

Punjab Salt Range, India.[25]

[11] CREDNER, *op. cit.*, pp. 503–11.

[12] GEIKIE, *op. cit.*, p. 853.

[13] Texas Survey, *Third Annual Report*, p. 212.

[14] *University Geological Survey of Kansas*, Vol. V.

[15] U. S. Geological Survey, DARTON's report, *loc. cit.*

[16] *Geological Survey of Michigan*, Vol. V (1881–93), Part II, pp. 14–30.

[17] *Mineral Resources of Canada*, 1897, pp. 105–11.

[18] *Resources of Southwestern Virginia*, Boyd, 1875, pp. 260–304. The reference of Virginia gypsum to the Lower Carboniferous is exceedingly doubtful.

[19] U. S. Geological Survey, *Benton Folio*, p. 6.

[20] GEIKIE, *op. cit.*, p. 789.

[21] *New York Geological Survey*, Vol. III, No. 15, p. 550.

[22] *Geological Survey of Ohio*, Vol. VI, pp. 691–702.

[23] Geological Survey of Pennsylvania, *Summary Final Reports*, Vol. II, pp. 913–15.

[24] *Geological Survey of Michigan*, Vol. I (1869–73), Part III, pp. 29–31.

[25] GEIKIE, *op. cit.*, pp. 737–39.

Climatic conditions in both hemispheres, therefore, seem to have been favorable for deposits of gypsum during the Permian, whereas, if the Iowa gypsum were referred to the Cretaceous, it would be the only gypsum deposit of economic importance in Europe or America assigned to this period of geological history. The gypsum may therefore be reasonably regarded as Permian, though the possibility of its being Triassic cannot be denied.

ORIGIN OF THE GYPSUM.

Gypsum deposits are generally ascribed to two causes: (1) the transformation of deposits already formed by various chemical reactions, and to reactions between the salts in solution, or (2) to precipitation from sea water, due primarily to concentration by evaporation.

1. The most frequent transformation of deposits already formed is the change of limestone ($CaCO_3$) into gypsum ($CaSO_4 + 2\ H_2O$), through the agency of sulphuric acid, according to the equation $H_2SO_4 + CaCO_3 = CaSO_4 + CO_2 + H_2O$. The sulphuric acid may be generated by the oxidation of the sulphuretted hydrogen of sulphur springs or of volcanoes, or by the action of water on some sulphide ore like pyrites. The deposits which Dana attributes to the action of sulphuric acid generated from the sulphuretted hydrogen given off by sulphur springs in New York[1] are quite extensive. In certain instances the gypsum occurs in masses with irregular outline in limestone, and layers of shale in the limestone pass unaltered through the gypsum. In view of this evidence, the gypsum must be regarded as derived from the limestone. Deposits of this sort are exceptional, however, and it is probable that most of the gypsum of New York had a different origin.

Insignificant gypsum deposits occur about the fumaroles of craters and lava streams in Hawaii where sulphurous acid SO_2 is converted into sulphuric, and attacks rocks which contain lime. The frequent occurrence of small amounts of gypsum with hematite in the upper part of ore veins may be accounted for by the following reaction;[2] $Fe_2O_3\ (SO_3)_2 + 2\ CaCO_3 = 2\ CaSO_4$

[1] DANA, *Manual of Geology*, 4th ed., p. 554. [2] BECK, *Erzlagerstattenlehre*, p. 393.

$+ Fe_2O_2 + 2\ CO_2$, the original form of the iron being FeS_2. Cerussite and smithsonite with gypsum in a mineral vein are similarly accounted for. Anhydrite when exposed to air containing moisture gradually takes on water and forms gypsum.

2. That great quantities of gypsum in all parts of the world and at different times in geological history have been derived from sea water by evaporation is generally recognized. Sea water contains 3½ per cent. of mineral matter, distributed as follows:

Chloride of sodium	77.758%
Chloride of magnesium	10.878
Sulphate of magnesium	4.737
Sulphate of calcium (gypsum)	3.600
Sulphate of potassium	2.465
Carbonate of lime	0.345
Bromide of magnesium	0.217
Total	100.000%

Gypsum is deposited from typical sea water when 80 per cent. of the water has evaporated, whereas common salt is not deposited until the bulk of the water is reduced more than 90 per cent. Gypsum deposits are more widespread than salt, but salt usually occurs in thicker beds. These facts, taken with the relative amount of each salt in sea water and the amount of evaporation necessary for precipitation in each case, accord with the theory which regards the evaporation of sea water as the cause of most salt and gypsum deposits. It is evident that conditions allowing the 80 per cent. of evaporation necessary for a gypsum deposit would occur more often than those giving rise to 90 per cent. of evaporation and a deposit of rock salt. When the amount of evaporation necessary for a salt deposit took place, however, the high percentage of salt in the water would yield a stratum of notable thickness as compared with gypsum.

The accompanying diagram indicates the relation of deposition to density in the case of the salts common to sea water. The magnesium chloride alone is not actually precipitated, but remains in solution always under ordinary atmospheric conditions. It may be precipitated, however, with potassium chloride as carnallite. Three-fourths of the gypsum is deposited between

the densities of 1.1315 and 1.21, whereas the deposition of salt does not begin until the latter point is reached. The remaining one-fourth is precipitated with the salt, but constitutes so small a part of the whole that the commercial value of the salt is not appreciably lowered. The normal order of deposition on evaporation from sea water, beginning with the first which occurs, of course, at the bottom of the deposit, is:

1. Limestone with limonite, $CaCO_3$ and $2Fe_2O_3$ $3H_2O$.
2. Gypsum $CaSO_4$ $2H_2O$.
3. Sodium chloride (common salt) NaCl.
4. The bitter salts (in carnallite) KCl $MgCl_2$ $6H_2O$.

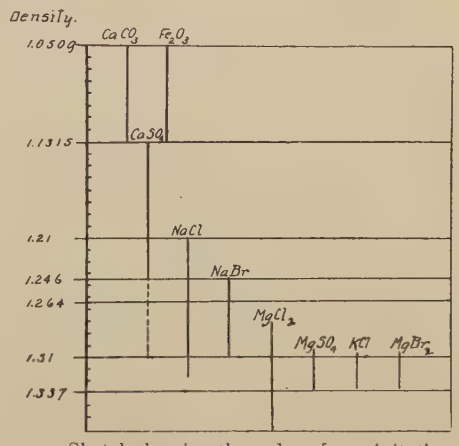

FIG. 1.—Sketch showing the order of precipitation of salts from sea water, with increase in density due to evaporation.

Practically this order is observed in the great salt deposits of Stassfurt, Germany.

While gypsum has been formed and is still forming in all of the ways described, most of these explanations are manifestly not adapted to the Webster county deposit. The definite lamination and layering of the gypsum indicate an aqueous origin. Pointing to the same conclusion is the fact that no limestones are associated with the gypsum which by alteration could yield gypsum. Salt may be regarded as absent from the Iowa gypsum area. If it existed, it would probably have been detected in some of the many wells and prospect holes. Its absence is not surprising, for the degree of concentration necessary for a salt deposit may never have been reached, or the salt, after having been deposited, may have been removed by subsequent erosion and solution.

The great thickness of some occurrences of gypsum and salt must be considered in seeking to determine their origin. The

combined series of Strassfurt amounts to more than 1,000 feet, and at Sperenberg to more than 3,000 feet. To yield even fifteen

FIG. 2.—Interior of Crawford mine. The bedding and lamination of the gypsum show nicely in the pile in the foreground, and in the wall behind the men.

feet of gypsum, the average thickness in the Iowa field, an immense amount of water must have been evaporated. A cubic foot of gypsum weighs 140 pounds, and the amount of gypsum

in a cubic foot of sea water today is three-fiftieths of one pound. The amount of water necessary to yield a cubic foot of gypsum, then, is 2,333.3 cubic feet. If the sides of the containing basin were vertical, the depth of the water necessary to produce fifteen feet of gypsum must have been 35,000 feet. If the average thickness of the Iowa gypsum be taken as fifteen feet and the gypsum area seventy square miles in extent, the amount of sea water necessary to deposit it, assuming that its content of gypsum was the same as in sea water today, was sixty-eight trillions of cubic feet. If a basin twenty miles wide be assumed, with two shores sloping to a center at an angle of 10 degrees, the length of the basin which would contain this amount of water must have been twenty-six miles and the depth at the center more than 9,000 feet, diminishing uniformly in depth from the center. Such a trough manifestly did not exist at the locality in question at the time of the deposition, and the hypothesis that the gypsum was deposited in a detached arm of the ocean, unaided by considerable supplies of salt from rivers or from the main body of salt water, is untenable.

There remain to be considered: (1) arms of the sea which were at least part of the time connected with the ocean, and which received more or less water from land; (2) inclosed seas fed wholly by rivers and without outlet except by evaporation.

Taking up the second case first, it will be instructive to review the conditions actually existing in inclosed salt seas in Asia and America. *The nature of salt deposits made in a lake not connected with the ocean and without outlet*, where evaporation is as great as, or greater than, inflow, may vary as widely as do the relative proportions of salts in the inflowing streams. The variation in the nature and amount of salts carried in solution by different streams is a natural consequence of differences in the mineral constitution of their drainage areas. In the Elbe and Thames chlorides predominate[1] (in the latter with gypsum), and the evaporation of these waters would give rise to lakes containing a large percentage of common salt. In the Seine, sulphate of lime (gypsum) predominates, while the waters of the Rhine,

[1] T. Sterry Hunt, *Chemical and Geological Essays.*

Danube, and Aar contain small amounts of chlorides and large percentages of sulphates of lime and magnesia. The Loire contains in 100,000 parts 13.46 of solid matter, of which 35 per cent. is calcium carbonate, while two-thirds of the soluble salts are carbonate of soda. In nearly all rivers bicarbonate of soda is present in large quantities. The solubility of calcium carbonate in water which is in contact with the air at 16°C. is 0.0746 grains per liter, which is six times its solubility in pure unaërated water. The $CaCO_3$ is for the most part present as the bicarbonate $Ca(HCO_3)_2$, only 3 per cent. of it existing as normal carbonate.[1]

ANALYSES OF SALTS IN THE WATERS FROM AMERICAN RIVERS.[2]

(Parts per 1,000,000 of water.)

Constituents	Ottawa	St. Lawrence	Mississippi	Missouri
K Cl	1.60	2.20	Not given	Not given
NaCl	....	2.25	8.57	32.03
K_2SO_4	1.22	....	Not given	Not given
Na_2SO_4	1.88	12.29	Not given	Not given
$MgSO_4$	....	....	15.41	125.20
$CaSO_4$	....	....	....	9.93
$MgCO_3$	6.96	25.37	19.63	....
$CaCO_3$	24.80	80.83	94.56	189.35
Na_2CO_3	4.10	.61	....	....

The water of the river Jordan gives the following analysis:[3]

Sodium chloride (common salt)	0.35
Magnesium chloride	0.03
Calcium chloride	0.07
Calcium sulphate (gypsum)	0.04
Water	99.50

The waters of the Dead Sea are the result of concentration by evaporation of waters containing salt. Quoting Bishof:[4]

In spring when the streams are turbid with the particles of carbonate of lime and clay, mere mechanical deposits take place, for at this period, when

[1] CAMERON AND BRIGGS, *Journal of Physical Chemistry*, Vol. V, No. 8, p. 548.

[2] BAILEY WILLIS, in JOURNAL OF GEOLOGY, Vol. I, p. 508. The waters of the Mississippi and the Missouri were sampled in the autumn during low water, near their junction.

[3] BISCHOF, *Chemical and Physical Geology*, Vol. I. [4] *Loc. cit.*, p. 397.

large masses of water are carried into the Dead Sea, and the saline solution thereby diluted, while at the same time the evaporation is but slight, no common salt is deposited. During the ensuing warmer months the chemical deposition of common salt and carbonate of lime take place. Should the stream become turbid at this season in consequence of continued rain, deposits are formed which contain a less amount of common salt. In this way there must arise a constant alternation of different irregular layers of greater or less thickness. All these layers must contain gypsum, since in a water which contains so much chloride of magnesium as is present in the Dead Sea, gypsum, as we shall subsequently see, is dissolved with difficulty, as is also shown by the small proportion in which this salt exists in that sea.

Lake Elton, a brine pool of the Russian steppes, may once have had an oceanic connection. If this is true, the calcium carbonate and gypsum of the original sea water have been deposited, for the water now contains but small quantities of lime salts, but chlorides of sodium and magnesium with sulphide of magnesium are present in abundance.[1] Bischof describes the lake as follows:

> The Elton lake, whose greatest diameter is 20 and its smallest 16 versts, lies 19 feet below the level of the ocean. It has flat banks and may be waded through almost anywhere. On its margins and upon its bed there is almost everywhere crystalline salt. This forms layers from one to two inches in thickness which are separated from one another by layers of mud and earth. The streams which empty into it are eight in number. They all contain more or less salt, and consequently carry supplies of this substance into the lake. The most considerable among them is the Charisacha, which is also the only one which continues to flow during the whole year. In the loamy soil which surrounds the lake numerous small crystals of gypsum are imbedded.

A deposit of salt is formed in this lake every summer. In the winter and spring the water is diluted by the rivers which are then copious, and a layer of silt, probably carrying some gypsum, is formed. The decrease or complete disappearance of $CaSO_4$ from the water of Lake Elton into which it is being constantly conveyed by the Charisacha River, the waters of which have been analyzed, shows that the gypsum goes down with the salt.

Great Salt Lake in Utah furnishes an excellent example of salt deposits in a lake without oceanic connections. The present

[1] Analysis by Gobel, quoted by Bischof, *loc. cit.*, p. 404.

lake is but a remnant of the much larger Lake Bonneville, which was at one time fresh and was drained by a stream flowing into the Snake River. Its present salinity is high, the specific gravity of the water being 1.1[1] and its saline contents, varying with the seasons from 14 to 22 per cent., is distributed as follows, as shown in five analyses:[2]

Sodium chloride	90.7	79.1	65.9	81.3	80.5
Potassium chloride	....	....	14.1	....	....
Magnesium chloride	1.1	9.9	8.9	6.7	10.3
Sodium sulphate	8.2	6.2	8.1	8.5	5.4
Potassium sulphate	....	3.6	....	2.6	2.4
Calcium sulphate	....	0.6	1.5	0.9	1.4
Chlorine (in excess)	....	0.6	1.5	....	....

Russell regards the analysis made by E. Waller,[3] of water, taken from Great Salt Lake in August, 1892, as the most complete and satisfactory that has been published.

Analysis by E. Waller, expressed in grams in a liter:

Specific gravity, 1.156.

NaCl	192.86
K_2SO_4	8.75
Li_2SO_4	0.16
$MgCl_2$	15.04
$MgSO_4$	5.21
$CaSO_4$	8.24
Fe_2O_3 and Al_2O_3	0.004
SiO_2	0.018
Surplus SO_3	0.051
Total	230.333

In these analyses the absence or the very small content of calcium, both as sulphate and carbonate, is remarkable. Analyses of the fresh waters tributary to the lake show that the lake could accumulate its total content of calcium in eighteen years, while the accumulation period for the chlorine would be 34,200 years.[4]

[1] Specific gravity in

1850	Summer 1869	Aug. 1873	Aug. 1889	Aug. 1892
1.17	1.111	1.102	1.157	1.156

—Compilation by RUSSELL, *Lakes of North America*, p. 81

[2] U. S. Geological Survey, *Monographs*, "Lake Bonneville," p. 254.

[3] *School of Mines* (Columbia College) *Quarterly*, Vol. XIV (1892), p. 58.

[4] U. S. Geological Survey, *Monographs*, "Lake Bonneville," p. 256.

Manifestly the lake is disposing of the calcium as fast as it is received. Deposits of tufa occur on the old Bonneville, Intermediate, and Provo shore lines, on their weather faces, and a few feet below their crests. It is absent in sheltered bays and most abundant on points that were especially exposed to wave action. Calcareous oölitic sands are now forming along certain parts of the shore of Salt Lake "between the delta of the Jordan and Black Rock, where it constitutes the material of a beach, and is drifted shoreward in dunes."[1] Of the three important fresh-water tributaries of Great Salt Lake, the water of Utah Lake is characterized by sulphate of lime, over 60 per cent. of the total solids held in solution by it consisting of this salt, while the waters of Bear River and City Creek are characterized by carbonate of lime.[2] The deposits of tufa and oölite alone may account for the absence of calcium carbonate from the water of the Great Salt Lake, yet it is possible that both the calcium carbonate and sulphate are precipitated in the ordinary manner by evaporation. Yet the fact that the calcium carbonate is, at least in a measure, taken from the water by the aëration due to wave action and deposited on the shores as tufa and oölite is interesting and, taken with other conditions, may account for deposits of pure gypsum from waters which contain a certain amount of lime carbonate.

Basins which are in some degree connected with the ocean may next be considered. The Bessarabian coast of the Black Sea furnishes an example of salt deposits in bays slightly connected with the open sea and fed from the landward side by rivers. From the Danube to the Dnieper the rivers before emptying into the ocean expand into lakes which are separated from the sea by natural dams. Under ordinary circumstances the water flows into the sea through an opening in the dam, while during storms the water of the sea enters the lakes. Three of these lakes become partially dry every summer and deposit salt which in places amount to a layer a foot thick.[3] This salt is used for commercial purposes. The calcium sulphate of the river water and of the sea water which is driven in during storms must also be deposited, but the quantity, being small, readily escapes notice.

[1] *Ibid.*, p. 169. [2] *Ibid.*, p. 207. [3] BISCHOF, *op. cit.*, Vol. I, p. 392.

Many writers on gypsum and salt have called attention to the fact that the Mediterranean Sea furnishes conditions which, if but slightly modified, would result in deposits of these substances.[1] Although it receives the waters of many rivers, some of them of considerable size, evaporation takes place faster than inflow, and if no water entered through the Strait of Gibraltar, or if the supply entering were considerably reduced, much of the mineral matter held in solution would be deposited. A steady current pours in from the ocean, however, and the density necessary for precipitation is not reached. The bottom of the sea rises sharply near the Strait of Gibraltar, cutting off communication between the lower part of the sea and the ocean, but permitting a free interchange of water in the upper level. The depth at the strait is less than 200 fathoms, while the average depth of the Mediterranean is 1,000 fathoms. The accompanying diagram roughly illustrates existing conditions:

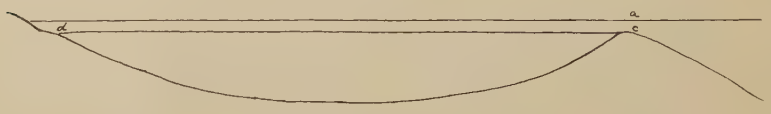

FIG. 3.

The amount of salt in the water of the Atlantic is 3.6 per cent., while in the Mediterranean it is 3.9 per cent. The specific gravity of the water of the Atlantic off the Strait of Gibraltar is 1.026, while at the west end of the Mediterranean, near the surface, it is 1.028, increasing in the east end to 1.03. At a depth of 300 fathoms the density is considerably greater than at the surface. A current of water flows in constantly at the surface of the strait (Fig. 3, *a*). This water is concentrated by evaporation and sinks. The bottom below the line *c d* has been previously filled by this dense water, and the water above this line is being constantly condensed and sinking causes a portion at the bottom water to flow out at *c* as a lower current into the ocean. The outlet at the strait is so free that the condensation does not reach the point which results in the deposition of lime, gypsum, or salt.

[1] *Geological Survey of Michigan*, Vol. V (1881–93), Part II, pp. 1–13; *University Geological Survey of Kansas*, Vol. 5, "Gypsum," Introduction.

It is quite conceivable that the opening could be so restricted that the outflow would be greatly diminished and the density of 1.05 to 1.13 which is necessary for the deposition of limestone be reached. If this were maintained for a long time and the outflow were enough to prevent further concentration, a thick bed of limestone without gypsum and salt would be formed. If the opening were still further restricted, gypsum would be precipitated and at length salt. In this case, however, the calcium carbonate in the inflowing sea water would be precipitated with the gypsum, unless converted into gypsum or a more soluble salt by reaction with other salts, or isolated during deposition, as is the case today in Great Salt Lake. The amount of the calcium carbonate (one-tenth as much as the gypsum), if present, would be easily recognized. If, instead of a small opening, the inland sea were shut off from the ocean by a low barrier, over which the sea water passed only in time of great storms, the deposits might be more varied. The water would be diluted at times so that precipitation of the more soluble salts would cease, and after a period of evaporation, if the amount of calcium carbonate in the newly added water were considerable, there would be a deposit of limestone succeeded by gypsum. A series of limestone and gypsum beds occurs in the northern peninsula of Michigan near St. Ignace.

In applying "inclosed sea" conditions like those now prevailing about Great Salt Lake to the Iowa gypsum, two questions arise. Was there a supply of gypsum in the rocks of the region subject to the solvent action of stream water sufficient to yield the existing deposit? If this question may be answered in the affirmative, do the deposits formed in inclosed seas structurally and chemically resemble those of Webster county? The Coal-Measure shales and sandstones, with here and there a limited area of St. Louis limestone, formed the land surface when the gypsum was deposited. There is a considerable amount of gypsum in all of these strata which appears frequently in large selenite crystals. Rivers flowing over this surface would carry a large percentage of gypsum in solution, provided the gypsum now contained in these strata was present at that time. It is

hardly probable that the gypsum of the Coal-Measure shales was formed at the time of their deposition, for the presence of great numbers of ferns indicate fresh water. A more probable origin lies in the action of water on pyrites, giving rise to ferrous sulphate, which in turn changed part of the lime carbonate of the shales into gypsum. This may have taken place before the great gypsum deposit was made, and, if so, the gypsum dissolved out of the Coal-Measure shales may have been sufficient to form it. The same waters which carried the gypsum would, however, carry much lime carbonate and mud, and it is difficult to conceive of fifteen feet of pure gypsum forming in an inclosed basin fed by streams. It is true that at the top in one or two localities thin layers of limestone, sandstone, or shale occur with thin layers of gypsum, but the presence of fifteen feet of gypsum containing only 1 per cent. of sand and clay practically precludes the possibility of its origin in an inland basin fed by land streams.

Turning to the "Mediterranean hypothesis," there are two apparent difficulties. In the series of deposits due to deposition on account of evaporation in such a basin, limestone would be the lowest member. If the amount of calcium carbonate in the waters tributary to the basin was small, limestone might not appear beneath the gypsum as a distinct formation, but, mixed with the finer impurities, would still be present as a notable calcareous element in a clay or shale. The Iowa gypsum overlies a fire clay, the analysis of which shows but a very limited amount of lime. Moreover, the lime carbonate in the inflowing water, after the density necessary for the deposition of gypsum had been reached in the basin, would, it would seem, be deposited with the gypsum. The phenomena observed about Great Salt Lake perhaps relieve us of these difficulties. As already stated, the water of the lake is almost free from calcium carbonate, while deposits of calcareous tufa and oölite have been and still are forming along the shores where water action is violent. This localizing of the calcium carbonate, if it were complete, would render possible deposits of pure gypsum like that of Iowa, in which no calcium carbonate appears. Unfortunately, calcium carbonate due to precipitation from solution appears widely dis-

tributed in the marl of the old Bonneville bed, as well as along the shore.[1] Still, the fact that calcium carbonate deposits were favored at the shores by the aëration associated with wave action is particularly significant. Even more significant is the fact that near the streams which contribute to the lake the greatest amount of lime carbonate, the calcareous oölite already mentioned, accumulates as a shore deposit in considerable quantities. If in this or some similar way the lime carbonate was localized, the Mediterranean hypothesis would appear satisfactory.

The experiments of Thoulet, quoted by Bailey Willis,[2] seemed to show that carbonate of lime in the form of marble, shells, coral, and globigerina ooze are much less soluble in ocean water than in fresh water. If this is true, when river water enters a salt sea, conditions for unstable equilibrium of the bi-carbonate of lime might arise which would result in the formation, and probably the deposition, of the neutral carbonate, and the greater the salinity of the sea, the more prompt and complete would be the precipitation. In this way streams on entering a salt sea might precipitate all of their calcium carbonate near their mouths, while gypsum would be deposited on subsequent evaporation in more remote parts of the basin. Willis calls attention to the limestone deposited beyond the delta of the Rhone. He says:[3]

> This is referred to by Thoulet and described by Lyell who says: "In the Museum at Montpelier is a cannon taken up from the mouth of the river imbedded in crystalline calcareous rock. Large masses also are continually taken up of an arenaceous rock cemented by calcareous matter, including multitudes of broken shells of recent species." Lyell attributes the precipitation of lime to the evaporation of the Rhone water, which, when it is spread upon the salt water, he compares to a lake. But this one cause is no doubt combined with the chemical and mechanical conditions which have been suggested in the preceding discussion. These conditions are favored at the mouth of the Rhone by the salinity of the Mediterranean and the absence of strong currents.

The experiments of Cameron and Seidell[4] gave results which differ radically from those of Thoulet. These chemists found

[1] U. S. Geology Survey, *Monograph 2*, "Lake Bonneville," p. 190.

[2] JOURNAL OF GEOLOGY, Vol. I, p. 510. [3] *Ibid.*, p. 516.

[4] CAMERON AND SEIDELL, in *Journal of Physical Chemistry*, Vol. VI, No. 1, p. 52.

that a maximum solubility for calcium carbonate was reached in a solution holding 50 grams of sodium chloride per liter, when its solubility was 2.36 times greater than in water without sodium chloride, but in equilibrium with air. In view of these experiments, which were conducted with great care, the experiments of Thoulet and the conclusions based on them must be questioned.

It is possible also to assume that chemical reactions took place between the salts in solution, which resulted in the elimination of this lime carbonate, by converting it either into gypsum or into a salt that is more soluble than gypsum, thus keeping it in solution until after the gypsum was deposited. It is well known that reactions between various salts contained in sea water may causes divergence from the series which results from evaporation alone. According to Usiglio, sea water deposits limestone abundantly when the density reaches 1.0506, and again at 1.1304. The last deposit he ascribes to the decomposition of sodium carbonate and gypsum with the formation of sodium sulphate and calcium carbonate.[1] Oschenius holds that sudden and well-marked deposits of gypsum may be caused by the addition of sodium or calcium chloride.

The solubility of gypsum in a sodium-chloride solution increases with the strength of the solution, as shown in the following table by Cameron:[2]

NaCl AND $CaSO_4$ IN WATER AT 150° C.

Grams NaCl per Liter	Grams $CaSO_4$ per Liter
0.6	2.3
1.1	2.5
5.1	3.1
10.6	3.7
31.1	4.8
51.4	5.6
139.9	7.4

So when the solution contains 140 grams of the NaCl per liter, the solubility of $CaSO_4$ is more than three times as great as in water without sodium chloride. In solutions containing less than

[1] HUBBARD, *Geological Survey of Michigan*, Vol. V, Part II, pp. 1–33.

[2] *Journal of Physical Chemistry*, Vol. V, No. 8, p. 559.

140 grams of NaCl per liter the solubility of gypsum is affected but slightly by changes of temperature. In a sodium-chloride solution the presence of calcium carbonate up to 8–10 per cent. is scarcely a factor in determining the amount of gypsum that will be dissolved.[1]

At low temperature in Salt Lake a double decomposition takes place between magnesium sulphate and sodium chloride, resulting in the formation of sodium sulphate which is deposited and magnesium chloride which remains in solution.[2]

All of the facts cited in regard to the solubility of gypsum and calcium carbonate in mixed solutions and double decompositions probably have little bearing on chemical deposits from sea water, though they might be determining factors in the order of deposition in inland lakes. Assuming that the composition of sea water in the past did not differ greatly from that of the present, in the course of its evaporation there is little reason for supposing a departure from the normal order of precipitation found in all salt pans where sea water is used. If a marked difference in composition existed, however, it might become a prime factor in the problem. Given an excess of sulphates (such as Na_2SO_4); or an excess of calcium ions (as regards calcium carbonate) from calcium sulphate, and it *may* be found that the curves plotted to illustrate the solubility of calcium carbonate and calcium sulphate in mixed solutions, will cross each other in such a way as to allow the calcium sulphate (gypsum) to come down first.

A change in the amount of atmospheric carbon dioxide, or a considerable change in temperature, might seriously change the order of deposition from that which now occurs when sea water is evaporated under ordinary conditions. A further study of these conditions during periods of great gypsum deposition may make clear the reason for vast deposits of gypsum due to evaporation of sea water which contain at the most only traces of calcium carbonate.

The same line of reasoning which is used to explain great

[1] CAMERON AND SEIDELL, in *Journal of Physical Chemistry*, Vol. V, No. 9, p. 653.

[2] RUSSELL, *Lakes of North America*, p. 75.

deposits of gypsum may be applied to many limestones. Calcium carbonate in sea water is one-tenth as abundant as calcium sulphate, and for every twenty feet of gypsum two feet of limestone must be precipitated, unless the calcium carbonate is converted into some other substance. Since the density required to precipitate limestone is far below that required for deposition of gypsum, it is highly probable that in many shallow seas but slightly connected with the abyssmal ocean limestone was continuously and abundantly deposited. Such deposits must be more wide-spread than gypsum, for the same reasons that gypsum deposits must be more abundant than salt. While laying stress on this point, the fact probably remains that most of the limestone of the earth is of organic origin.

While conditions like those now existing in the Mediterranean Sea, when somewhat intensified, may in the main be regarded as giving rise to gypsum deposits, this sea presents one peculiarity which could not have characterized many of the regions where gypsum occurs. Structural conditions indicate that most of the gypsum deposits were formed in arms of a shallow epi-continental sea. The Mediterranean Sea with its average depth of 1,000 fathoms is truly abyssmal.

Although there may be some doubt as to the exact manner in which the calcium carbonate is removed from the brine during concentration, the fact that it is removed in some one or more of the ways suggested, or by some process not yet brought to light, may be assumed. This removes the only serious difficulty in conceiving of extensive and very pure deposits of gypsum forming in basins only slightly, yet continuously through long periods, connected with the ocean. The Mediterranean hypothesis, with the modifications pointed out, may be accepted as accounting for the Iowa gypsum, as well as similar deposits in various periods of geological history. It must be admitted, however, that further chemical investigations in regard to the reactions between salts in solution during the process of brine concentration must be undertaken before the problem can be regarded as fully solved.

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